International Standard ISO 7099

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Phosphoric acid for industrial use (including foodstuffs) — Determination of hydrogen sulfide content — Titrimetric method

Acide phosphorique à usage industriel (y compris les industries alimentaires) — Dosage du sulfure d'hydrogène — Méthode titrimétrique.

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Foreword

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Phosphoric acid for industrial use (including foodstuffs) — Determination of hydrogen sulfide content — Titrimetric method

1 Scope and field of application

This International Standard specifies a titrimetric method for the determination of the hydrogen sulfide content of phosphoric acid for industrial use (including foodstuffs).

The method is applicable to products having hydrogen sulfide contents, expressed as H_2S, greater than or equal to 0,05 mg/kg.

2 References

ISO 4285, *Phosphoric acid for industrial use — Guide to sampling techniques.*

ISO 6228, *Chemical products for industrial use — General method for determination of traces of sulfur compounds, as sulfate, by reduction and titrimetry.*

3 Principle

Removal of the hydrogen sulfide in a test portion in a stream of nitrogen and absorption in a solution of sodium hydroxide in aqueous acetone. Titration of the sulfide ions with standard volumetric mercury(II) acetate solution, in the presence of 1,5-diphenylthiocarbazone (dithizone) as indicator.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity, boiled to eliminate dissolved oxygen and cooled in a current of the nitrogen (4.2).

4.1 Acetone.

4.2 Nitrogen, free from oxygen, in a cylinder provided with a pressure-release valve.

4.3 Phosphoric acid, ϱ 1,75 g/ml, approximately 85 % (m/m) solution.

4.4 Sodium hydroxide, 40 g/l solution.

4.5 Sodium sulfide, standard reference solutions.

4.5.1 Sodium sulfide, standard solution corresponding to approximately 1,70 g of H_2S per litre.

4.5.1.1 Preparation

Rinse some crystals of sodium sulfide nonahydrate ($Na_2S.9H_2O$) with water on a coarse sinter to remove surface deposits of sulfite. Dry the crystals between filter paper and, without delay, weigh about 3,3 g of the product into a 100 ml beaker containing water. Transfer the solution to a 250 ml one-mark volumetric flask previously swept out with the nitrogen (4.2). Dilute to the mark and mix.

4.5.1.2 Standardization

Transfer 25,00 ml of a standard volumetric solution of iodine, $c(1/2\ I_2) = 0{,}1$ mol/l, to a 250 ml iodine flask containing 20 ml of the phosphoric acid solution (4.3). Stopper the flask and cool under running water. When cold, add 20,0 ml of the sodium sulfide solution (4.5.1.1), keeping the tip of the pipette below the surface of the liquid, and mix. Titrate the excess iodine with a standard volumetric sodium thiosulfate solution, $c(Na_2S_2O_3.5H_2O) = 0{,}1$ mol/l, using soluble starch as the indicator.

4.5.1.3 Blank test

Carry out a blank test, using the same volumes of the phosphoric acid solution (4.3) and of the standard volumetric iodine solution and titrating with the standard volumetric sodium thiosulfate solution, but omitting the addition of the sodium sulfide solution.

4.5.1.4 Calculation of the concentration

The concentration c, expressed in milligrams of H_2S per millilitre, of the sodium sulfide solution is given by the formula

$$\frac{V_0 - V_1}{20} \times 1{,}703$$

$$= 0{,}085\ 15\ (V_0 - V_1)$$

where

V_0 is the volume, in millilitres, of the standard volumetric sodium thiosulfate solution used for the blank test (4.5.1.3);

V_1 is the volume, in millilitres, of the standard volumetric sodium thiosulfate solution used to titrate the excess iodine added to the sodium sulfide solution (4.5.1.1);

1,703 is the mass, in milligrams, of hydrogen sulphide corresponding to 1,00 ml of a sodium thiosulfate solution $c(Na_2S_2O_3).5H_2O) = 0{,}100$ mol/l;

20 is the volume, in millilitres, of the sodium sulfide solution (4.5.1.1) taken for the standardization (4.5.1.2).

NOTE — This solution is not stable. Store it in a tightly stoppered flask swept out with the nitrogen (4.2). Discard the solution after 3 days.

4.5.2 Sodium sulfide, standard solution corresponding to 70 mg of H_2S per litre.

Take a volume, in millilitres, of the sodium sulfide solution (4.5.1) corresponding to 35,0 mg of H_2S, given by the formula

$$\frac{35{,}0}{c}$$

where c is the concentration calculated in 4.5.1.4.

Transfer to a 500 ml one-mark volumetric flask previously swept out with the nitrogen (4.2), dilute to the mark and mix.

Prepare the solution immediately before use.

4.5.3 Sodium sulfide, standard solution corresponding to 3,5 mg of H_2S per litre.

Transfer 10,00 ml of the freshly prepared sodium sulfide solution (4.5.2) to a 200 ml one-mark volumetric flask previously swept out with the nitrogen (4.2), dilute to the mark and mix.

Prepare the solution immediately before use.

4.6 Mercury(II) acetate, standard volumetric solutions.

4.6.1 Mercury(II) acetate, standard volumetric solution, $c[Hg(CH_3COO)_2] = 0{,}05$ mol/l.

Weigh, to the nearest 0,000 1 g, 1,593 5 g of mercury(II) acetate and dissolve in water in a 100 ml beaker. Transfer the solution quantitatively to a 100 ml one-mark volumetric flask, dilute to the mark and mix.

4.6.2 Mercury(II) acetate, standard volumetric solution, $c[Hg(CH_3COO)_2] = 0{,}001$ mol/l.

Transfer 10,00 ml of the mercury(II) acetate solution (4.6.2) to a 500 ml one-mark volumetric flask, dilute to the mark and mix.

4.6.3 Mercury(II) acetate, standard volumetric solution, $c[Hg(CH_3COO)_2] = 0{,}000\,1$ mol/l.

Transfer 25,00 ml of the mercury(II) acetate solution (4.6.2) to a 250 ml one-mark volumetric flask, dilute to the mark and mix.

Prepare this solution immediately before use.

NOTE — In view of the low sulfide contents to be determined, the concentrations of the solutions (4.6.1, 4.6.2 and 4.6.3) are sufficiently exact and standardization is therefore unnecessary.

4.7 1,5-Diphenylthiocarbazone [Dithizone], 0,5 g/l solution in the acetone (4.1).

Discard the solution after 15 days.

5 Apparatus

See clause 5 of ISO 6228, but provide several microburettes (5.2).

6 Sampling

Sampling shall be carried out in accordance with the requirements of ISO 4285.

7 Procedure

7.1 Test portion

Weigh, to the nearest 0,01 g, a mass of the laboratory sample (see clause 6) containing 1,5 to 100 µg of H_2S but weighing not more than 30 g, and transfer to the reduction flask of the apparatus (5.1).

7.2 Check test

Pour into the receiver of the apparatus (5.1) 5 ml of the sodium hydroxide solution (4.4), 5 ml of the acetone (4.1) and 0,1 ml of the dithizone solution (4.7). Mix and add, drop by drop, the appropriate mercury(II) acetate solution (see the table in 7.3) to the first pink coloration.

Transfer to a second reduction flask of the apparatus (5.1) 50 ml of water and 20 ml of the phosphoric acid solution (4.3). Assemble the apparatus as shown in the figure in ISO 6228, having first smeared the ground glass cones lightly with silicone grease and fitted them with suitable clips to ensure gas tightness.

Pass a current of oxygen-free nitrogen (4.2) gently through the inlet tube at about 10 l/h for 12 min.

Disconnect the connecting tube at the spherical joint, lower the receiver and allow the connecting tube to drain into the receiver. Raise the receiver and allow the solution to rise into the connecting tube, then lower the receiver so that the connecting tube empties once more. Repeat this sequence of operations several times in order to wash out the inside of the connecting tube. Finally, rinse out the connecting tube with a little acetone (4.1) to bring the volume of the absorption solution to 10 to 11 ml.

Add, drop by drop, from a microburette (5.2), mercury(II) acetate solution (4.6) of the same concentration as that already used to regain the pink coloration. Do not add an excess.

Transfer to the reduction flask from a microburette (5.2) 2,00 ml of the sodium sulfide solution of the appropriate concentration (see the table in 7.3), keeping the burette tip below the surface of the liquid. At once reassemble the apparatus (5.1) and continue as from the third paragraph of this clause, "Pass a current of oxygen-free nitrogen...", ending by titrating the absorption solution [with the standard volumetric mercury(II) acetate solution, from a microburette, to regain the pink coloration].

The percentage recovery of H_2S is given by the formula

$$\frac{V_2 \times m_0 \times 100}{2{,}00 \times m_1}$$

where

V_2 is the volume, in millilitres, of the standard volumetric mercury(II) acetate solution used for the last titration;

m_0 is the mass, in micrograms, of H_2S corresponding to 1 ml of the mercury(II) acetate solution used;

m_1 is the mass, in micrograms, of H_2S corresponding to 1 ml of the sodium sulfide solution used.

The check test is considered satisfactory if the value is 90 % or better.

If it is less than this, check the following parameters :

a) the gas tightness of the apparatus;

b) the time given for displacement of H_2S;

c) the nitrogen flow rate.

7.3 Determination

Transfer to the receiver 5 ml of the sodium hydroxide solution (4.4), 5 ml of the acetone (4.1) and 0,1 ml of the dithizone solution (4.7). Mix and add, drop by drop, the appropriate standard volumetric mercury(II) acetate solution (see the table), to the first pink coloration.

Expected mass of hydrogen sulfide in test portion	Standard volumetric mercury(II) acetate solution to be used	Standard reference sodium sulphide solution to be used for checking apparatus (7.2)
µg		
1,5 to 15	4.6.3	4.5.3
15 to 100	4.6.2	4.5.2

Add 50 ml of water to the test portion in the reduction flask and assemble the apparatus as shown in the figure in ISO 6228, having first smeared the ground glass cones lightly with silicone grease and fitted them with suitable spring clips to ensure gas tightness.

Continue as described in 7.2, from the third paragraph, "Pass a current of oxygen-free nitrogen,,," to "to bring the volume of the absorption solution to 10 to 11 ml."

Titrate the absorption solution with the standard volumetric mercury(II) acetate solution (4.6) of the same concentration as that already used, from a microburette (5.2), to the first pink coloration.

8 Expression of results

The hydrogen sulphide content, expressed in milligrams of H_2S per kilogram, is given by the formula

$$\frac{V_3 \times m_0}{m_2}$$

where

V_3 is the volume, in millilitres, of the standard volumetric mercury(II) acetate solution used for the determination (7.3);

m_0 has the same meaning as in 7.2;

m_2 is the mass, in grams, of the test portion (7.1).

9 Test report

The test report shall include the following particulars :

a) an identification of the sample;

b) the reference of the method used;

c) the results and the method of expression used;

d) any unusual features noted during the determination;

e) any operation not included in this International Standard or in the International Standards to which reference is made, or regarded as optional.

Annex

ISO publications relating to phosphoric acid for industrial use

ISO 848 — Determination of calcium content — Titrimetric method.

ISO 849 — Determination of iron content — 2,2'Bipyridyl photometric method.

ISO 2997 — Determination of sulfate content — Method by reduction and titrimetry.

ISO 3359 — Determination of arsenic content — Silver diethyldithiocarbamate photometric method.

ISO 3360 — Determination of fluorine content — Alizarin complexone and lanthanum nitrate photometric method.*

ISO 3361 — Determination of soluble silica content — Reduced molybdosilicate spectrophotometric method.

ISO 3706 — Determination of total phosphorus(V) oxide content — Quinoline phosphomolybdate gravimetric method.*

ISO 3707 — Determination of calcium content — Flame atomic absorption method.*

ISO 3708 — Determination of chloride content — Potentiometric method.*

ISO 3709 — Determination of oxides of nitrogen content — 3,4-Xylenol spectrophotometric method.*

ISO 4285 — Guide to sampling techniques.

ISO 6678 — Determination of lead content — Atomic absorption spectrometric method.

ISO 7058 — Determination of higher soluble sulfate contents — Titrimetric method after reduction.

ISO 7099 — Determination of hydrogen sulfide content — Titrimetric method.*

ISO 7100 — Determination of vanadium content — Phosphotungsten vanadate spectrometric method.*

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* Also applicable to phosphoric acid fo ruse in the foodstuffs industry.